[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the lithium secondary battery which used the electrode for lithium secondary batteries, and this.
[0002]
[Description of the Prior Art] Development of a lithium secondary battery is performed briskly in recent years. The battery characteristics, such as charge and discharge voltage, the charge-and-discharge cycle length characteristic, and the preservation characteristic, are greatly influenced by the electrode active material for which a lithium secondary battery is used.
[0003] When silicon alloys lithium with lithium also in occlusion and the electrode active material which can be emitted, it is the substance which can carry out occlusion of the lithium and many things are examined from the theoretical capacity being large. However, since silicon carries out occlusion of the lithium by alloying, its expansion contraction of the volume accompanying a charge-and-discharge reaction is large. for this reason, an active material -- fine -- a charge-discharge cycle characteristic is bad and has come to be put in practical use by the Reasons of powdering and the exfoliation from a current collection object taking place.
[0004] [In order to solve the above-mentioned problem, improvement of the silicon as an active material is tried by doping impurities or using the alloyed powder end of (JP,H10-199524,A), silicon, and a different-species element into silicon, (JP,2000-243389,A), but] Still sufficient result is not obtained.
[0005] Moreover, the method of aiming at improvement in the cycle characteristic is also proposed by using an intermetallic compound with elements, such as silicon, metal, or half-metal as a *** active material (JP,H10-223221,A). However, only at considering it as an intermetallic compound simply, although a capacity maintenance rate improves, it is little substantially to improve the electric discharge capacity after a cycle. Since specific chemistry stoichiometry exists in an intermetallic compound as this cause, it is possible that initial electric discharge capacity decreases sharply rather than the case where the quantity of the element which carries out occlusion discharge decreased, and lithium in unit volume is used with that element simple substance. For example, if the density of Si atom which will carry out occlusion discharge of the lithium if it is Si3M structure (M is metal or half-metal) is a 75 atom % grade in the case of Si simple substance and is Si2M structure, it will decrease to a 67 atom % grade.
[0006] These people have found out that the electrode which deposited and formed the silicon thin film on the current collection object by the thin film formation methods, such as a CVD method and the spattering method, shows high charge-and-discharge capacity, and the outstanding charge-discharge cycle characteristic is shown.
[0007] The purpose of this invention is to offer the lithium secondary battery using the electrode for lithium secondary batteries and this which can raise a charge-discharge cycle

characteristic further in the electrode for lithium secondary batteries which deposited and formed the silicon thin film on the current collection object.

[0008]

[Means for solving problem] This invention is the electrode for lithium secondary batteries which was made to deposit the thin film which makes silicon a subject, and was formed on the current collection object. At least one sort of the element (however, except for copper (Cu)) of the IIIa fellows of the periodic law table 4 cycle, five cycles, and six cycles, IVa fellows, Va fellows, VIa fellows, VIIa fellows, VIII fellows, Ib fellows, and IIb fellows is characterized by the lining of the thin film which makes silicon a subject included on the surface at least.

[0009] As the above-mentioned element, specifically SUKANJIUMU (Sc), titanium (Ti), Vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), Cobalt (Co), nickel (nickel), zinc (Zn), yttrium (Y), JIRUKONIUMU (Zr), niobium (Nb), molybdenum (Mo), TEKUNECHIUMU (Tc), RUTENIUMU (Ru), rhodium (Rh), palladium (Pd), silver (Ag), A cadmium (Cd), run TANOIDO system element, hafnium (Hf), tantalum (Ta), tungsten (W), RENIUMU (Re), osmium (Os), indium (Ir), platinum (Pt), gold (Au), and mercury (Hg) are mentioned.

[0010] As the above-mentioned run TANOIDO system element, a lantern (La), cerium (Ce), PURASEOJIMU (Pr), neodymium (Nd), pro MECHIUMU (Pm), Samarium (Sm), europium (Eu), gadolinium (Gd), TERUBIUMU (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), TSURIUMU (Tm), ITTERUBIUMU (Yb), and lutetium (Lu) are mentioned.

[0011] Also in the above-mentioned element, especially, since the diffusion coefficient to the inside of silicon is high, the element of VIII fellows, Ib fellows, and IIb fellows is desirable. Specifically, they are iron, Cobalt, nickel, zinc, RUTENIUMU, rhodium, palladium, silver, cadmium, osmium, indium, platinum, gold, and mercury.

[0012] It is desirable to use at least one sort especially chosen from Cobalt, zinc, iron, JIRUKONIUMU, nickel, silver, and manganese as the above-mentioned element. It is desirable to use also in these at least one sort especially chosen from Cobalt, zinc, iron, JIRUKONIUMU, and nickel.

[0013] In this invention, even if the thin film which makes silicon a subject has few above-mentioned elements, it is contained on the surface. By containing the element on the surface, it is thought that the reaction of the thin film surface and an electrolysis solution can be inhibited.

[0014] Moreover, the above-mentioned element may be contained in the whole thin film. When this element contains in a thin film, it is thought that the quantity of expansion contraction of the thin film at accompanying a charge-and-discharge reaction can be decreased. moreover -- changing the mechanical physical properties of a thin film by containing the above-mentioned element in a thin film -- a thin film -- fine -- it is thought that powdering can be controlled. Moreover, since the amount of expansion contraction of a thin film can be decreased, the

stress which works on a current collection object from a thin film in the case of charge and discharge can be decreased, and it is thought that it can control that wrinkles occur on a current collection object. By controlling generating of the wrinkles of a current collection object, the volume capacity density at the time of assembling a battery can be raised.

[0015] Moreover, when the above-mentioned element contains in a thin film, stabilization of a thin film arises. For this reason, even if it carries out the above-mentioned element content, the fall of the rate of the quantity of the active material element per unit volume is controlled, or [moreover,] that the quantity of the active material element per unit volume is equally maintained when quantity of the element made to contain is made into the specific range [-- or] it increases. At this time, the electric discharge capacity per unit volume is also equivalent, or the value beyond it is acquired.

[0016] As for the above-mentioned element, in this invention, it is desirable to form the solid solution with silicon in a thin film. For example, when the above-mentioned element is Cobalt, it is desirable that silicon and not the intermetallic compound of Cobalt but silicon and the solid solution of Cobalt are formed, and Cobalt contains with the form of a solid solution.

[0017] Moreover, as for a solid solution, it is desirable that it is the solid solution of a non-equilibrium situation. Only germanium is known what forms silicon and a solid solution in an equilibrium situation, but the solid solution of the above-mentioned element and silicon exists only in a non-equilibrium situation.

[0018] For example, when an element is Cobalt, according to silicon and the 2 yuan constitutional diagram of Cobalt, silicon and Cobalt form various intermetallic compounds in the large range of a composition ratio. However, a possibility that a solid solution will not be formed in the large range of a composition ratio, but either will be formed only in the range contained slightly is only realized. Here, an intermetallic compound means the compound which has the specific crystal structure which metal combined by the specific ratio. Since a 2 yuan constitutional diagram is a thing based on an equilibrium situation, it cannot be judged whether from a constitutional diagram, the solid solution of a non-equilibrium situation of 2 yuan is formed. It is thought that it becomes possible about lithium occlusion and to emit without thin film structure collapsing also by a charge-and-discharge reaction, when a solid solution is a solid solution of a non equilibrium situation.

[0019] It is desirable still more desirable that it is 30 or less weight %, and the content in the thin film of the above-mentioned element is 20 or less weight %. If the content in the thin film of the above-mentioned element becomes high too much, since the charge-and-discharge capacity of a thin film falls, it is not desirable. Moreover, it is desirable still more desirable that it is 0.1 weight % or more, and the content in the thin film of the above-mentioned element is 1 weight % or more. If the content of the above-mentioned element decreases too much, a reaction with an electrolysis solution is inhibited and the effect of this invention of raising a

charge-discharge cycle characteristic may not fully be acquired. Therefore, it is desirable still more desirable that it is 0.1 to 30 weight %, and the content of the above-mentioned element is 1 to 20 weight %.

[0020] As for the content in the thin film of the above-mentioned element, it is desirable that it is below 17 atom %, although a Reason is not clear, if the content in the thin film of the above-mentioned element becomes high too much, condensation of the above-mentioned element will arise -- being easy -- it -- an active material layer -- line -- since it becomes easy to produce powdering, it is thought that the effect of an improvement of the cycle characteristic decreases.

[0021] As for the thin film in this invention, it is desirable that the break formed in the thickness direction desiccates pillar-shaped. Since the crevice exists in the circumference of a pillar-shaped portion, the stress by expansion contraction of the thin film accompanying a charge-and-discharge cycle is eased by this crevice, and it can control that the stress that a thin film exfoliates from a current collection object occurs. Therefore, an adhesion state with the current collection object in the bottom of a pillar-shaped portion can be kept good.

[0022] Moreover, in the thickness direction of a thin film, it is desirable that 1/2 or more portions of the thickness of a thin film are separated by the break pillar-shaped at least. Moreover, when unevenness is formed on the surface of the thin film and the break which uses the trough of this unevenness as an end is formed in the thin film, the break may be formed so that a pillar-shaped portion may contain at least one convex part on the surface of a thin film. In this case, the break may be formed so that two or more convex parts may be included.

[0023] The break formed in a thin film may be formed by the charge and discharge after the first time. Before such a case, for example, charge and discharge, unevenness is formed on the surface of the thin film, the break which uses the trough of unevenness on the surface of a thin film as an end by the charge and discharge after the first time may be formed, and the thin film may be separated by this break pillar-shaped.

[0024] The unevenness on the surface of a thin film may be formed corresponding to unevenness of the current collection body surface which is a foundation layer. That is, unevenness can be given on the surface of a thin film by forming a thin film on it using the current collection object which has unevenness on the surface.

[0025] It is 0.01-1 micrometer that it is 0.01 micrometers or more desirable still more preferably, and the surface coarseness Ra of a current collection object is 0.05-0.5 micrometer still more preferably. The surface coarseness Ra is provided in Japanese Industrial Standards (JIS B 0601-1994), for example, can be measured with a surface coarseness meter.

[0026] As for the surface coarseness Ra of a current collection object in this invention, it is desirable to have the relation of Ra<=t to thickness t of an active material thin film. Moreover, as for the average interval S of the surface coarseness Ra of a current collection object, and

the local summit of the mountain, it is desirable to have the relation of Ra>>S. The average interval S of the local summit of the mountain is provided in Japanese Industrial Standards (JIS B 0601-1994), for example, can be measured with a surface roughness meter.

[0027] Although the form in particular of the convex part of unevenness of a current collection body surface is not limited, it is desirable that it is a cone-like, for example. Moreover, as for the upper part part of a pillar-shaped portion, it is desirable that it is roundish (wore) in order to avoid concentration of the current in a charge-and-discharge reaction.

[0028] In this invention, the break of the thickness direction formed in a thin film may be formed by the charge and discharge after the first time, and may be beforehand formed before charge and discharge. Before assembling a battery, after expanding the volume of a thin film, it can be made to be able to contract, and can be made to form by the method of making it back-emit etc. of carrying out occlusion of the lithium etc. to the thin film of the electrode, as a method of making such a break forming in a thin film beforehand before charge and discharge. Of course, when the active material which does not contain lithium is used for a plus terminal, where occlusion is carried out, you may assemble lithium. Moreover, it is good also as a thin film separated by the break pillar-shaped by forming a thin film pillar-shaped using the resist film patterned by photo lithography.

[0029] Generally silicon is divided roughly into amorphous silicon and micro crystallite silicon, polycrystalline silicon, and single crystal silicon by crystalline difference. About ($520cm^{-1}$) one peak on the Raman spectroscopic analysis and corresponding to a crystalline region in amorphous silicon is not detected substantially. Both about ($520cm^{-1}$) one peak on the Raman spectroscopic analysis and corresponding to a crystalline region in micro crystallite silicon and about ($480cm^{-1}$) one peak corresponding to an amorphous field are detected substantially. Therefore, micro crystallite silicon consists of a crystalline region and an amorphous field substantially. About ($480cm^{-1}$) one peak on the Raman spectroscopic analysis and corresponding to an amorphous field in polycrystalline silicon and single crystal silicon is not detected substantially.

[0030] In this invention, a micro crystallite silicon thin film and an amorphous silicon thin film are desirable as a silicon thin film in which the above-mentioned element is contained. Moreover, as a thin film which makes silicon a subject in this invention, a silicon germanium alloy thin film is mentioned in addition to the above-mentioned silicon thin film. As a silicon germanium alloy thin film, a micro crystallite silicon germanium alloy thin film and an amorphous silicon germanium thin film are used preferably. The micro crystallite and the quality of amorphism of a silicon germanium alloy thin film can be defined like the above-mentioned silicon thin film. Silicon and germanium dissolve uniformly, and since a good result is obtained in this invention, all are considered that a result good also about the silicon

germanium alloy which are these alloys is obtained.

[0031] In this invention, although the method in particular of forming a thin film on a current collection object is not limited, a CVD method, the sputtering method, the vapor depositing method, a thermal-spraying method, or the plating method is mentioned, for example. Also in these thin film formation methods, a CVD method, the sputtering method, and the vapor-depositing method are used especially preferably.

[0032] The method of mixing the material gas which contains the above-mentioned element in the material gas of silicon in the case of a CVD method, decomposing this mixed gas, and forming a thin film as a method of making the above-mentioned element containing, into a thin film, for example is mentioned. Moreover, in the case of the sputtering method, the target of silicon and the target of the above-mentioned element are arranged side by side, and the method of forming a thin film is mentioned to it. In the case of the vapor-depositing method, the source of vapor deposition of silicon and the source of vapor deposition of the above-mentioned element are arranged side by side, and the method of forming a thin film is mentioned to it.

[0033] The current collection object used in this invention will not be limited especially if a thin film can be formed by good adhesion nature on it. As an example of a current collection object, at least one sort chosen from copper, nickel, stainless steel, molybdenum, tungsten, and tantalum is mentioned.

[0034] As for a current collection object, it is desirable that thickness is thin, and it is desirable that it is metallic foil. Copper is mentioned as a material in which it is desirable especially desirable that the current collection object is formed from lithium and the material which is not alloyed. As for a current collection object, it is desirable that it is copper foil, and it is desirable that the surface is copper foil by which surface roughening was carried out. Electrolysis copper foil is mentioned as such copper foil. Electrolysis copper foil is copper foil which copper is deposited on the surface of a drum, and is exfoliated and obtained in this by sending current, metal drums being immersed for example, into the electrolysis solution in which copper ion was dissolved, and rotating this. The surface roughening process and the surface treatment may be made by one side or both sides of electrolysis copper foil.

[0035] Moreover, you may be copper foil which copper was deposited on the surface of rolling copper foil by the electrolyzing method, and carried out surface roughening of the surface to it. Moreover, an intermediate layer may be formed on a current collection object, and a thin film may be formed on this intermediate layer. In this case, what contains the ingredient which is easy to diffuse in a thin film as an intermediate layer is desirable, for example, a copper layer is desirable. For example, the surface may use the current collection object in which the copper layer was formed on the nickel foil (electrolysis nickel foil etc.) by which surface roughening was carried out. Moreover, on nickel foil, by the electrolyzing method, copper may

be deposited and the nickel foil which carried out surface roughening by this may be used.
[0036] The break formed in a thin film in this invention may be beforehand formed along the low density field formed so that it might extend in the thickness direction into a thin film. Such a low density field is formed, for example so that it may extend toward the upper part from the trough of unevenness of a current collection body surface.
[0037] In this invention, it is desirable that the ingredient of a current collection object is spread in the thin film. Diffusion into the thin film of such a current collection object ingredient can raise the adhesion nature of a current collection object and a thin film. Moreover, since alloying with lithium is controlled in a diffusion field when elements, such as lithium and copper which is not alloyed, are spread as a current collection object ingredient, Expansion and contraction of the thin film accompanying a charge-and-discharge reaction can be controlled, and generating of stress which produces the exfoliation from the current collection object of an active material thin film can be controlled.
[0038] Moreover, as for the concentration of the current collection object ingredient diffused in the thin film, it is desirable to decrease as it is high and the thin film surface is approached near the current collection object. In order that control of expansion and contraction of the thin film accompanying a charge-and-discharge reaction may work more strongly [near the current collection object] by having the concentration gradient of such a current collection object ingredient, it becomes easy to control that the stress which produces exfoliation of an active material thin film occurs near the current collection object. Moreover, when the concentration of a current collection object ingredient decreases, high charge-and-discharge capacity is maintainable as the thin film surface is approached.
[0039] Moreover, as for the diffused current collection object ingredient, it is desirable to form the solid solution, without forming a thin film ingredient and an intermetallic compound into a thin film. Here, an intermetallic compound means the compound which has the specific crystal structure which metal combined by the specific ratio. When a thin film ingredient and a current collection object ingredient form not an intermetallic compound but a solid solution into a thin film, the adhesion state of a thin film and a current collection object becomes better, and higher charge-and-discharge capacity can be obtained.
[0040] Impurities other than the above-mentioned element may be doped by the thin film in this invention. As such impurities, elements, such as a phosphorus, aluminum, arsenic, antimony, boron, gallium, indium, oxygen, and nitrogen, can be mentioned, for example.
[0041] Moreover, the thin film in this invention laminates two or more layers, and may be formed. In the laminated each layer, composition, crystallinity, and the above-mentioned element may differ from the concentration of impurities etc. Moreover, you may have inclination structure in the thickness direction of a thin film. For example, composition, crystallinity, the above-mentioned element, concentration of impurities, etc. can be made into

the inclination structure where it was made to change in the thickness direction.

[0042] moreover -- the thin film in this invention -- beforehand -- lithium -- occlusion -- or you may be added. You may add lithium, when forming a thin film. That is, you may add lithium to a thin film by forming the thin film containing lithium. After [moreover,] forming a thin film -- a thin film -- lithium -- occlusion -- or you may make it add. Considering lithium as occlusion or a method of making it add, occlusion or the method of making it add is electrochemically mentioned to a thin film in lithium.

[0043] Moreover, although the thickness in particular of the thin film of this invention is not limited, it can be made into a thickness of 20 micrometers or less, for example. Moreover, in order to obtain high charge-and-discharge capacity, as for thickness, it is desirable that it is 1 micrometers or more.

[0044] The lithium secondary battery of this invention is characterized by having *** which consists of an electrode of above-mentioned this invention, a plus terminal, and nonaqueous electrolyte. [the solvent of the electrolyte used for the lithium secondary battery of this invention] Although not limited in particular, annular carbonate, such as ethylene carbonate, propylene carbonate, butylene carbonate, and vinylene carbonate, A mixed solvent with chain-like carbonate, such as dimethyl carbonate, methylethyl carbonate, and diethyl carbonate, is illustrated. Moreover, a mixed solvent with chain-like ether, such as ether system solvents, such as said annular carbonate, 1, and 2-dimethoxyethane, 1, and 2-diethoxy ethane, and gamma-butyrolactone, a sulfolane, acetic acid MECHIRU, etc. is also illustrated. As electrolytic ***, moreover, LiPF6, LiBF4, LiCF3SO3, LiN(CF3SO2)2, LiN(C2F5SO2)2, LiN (CF3SO2) (C4F9SO2), These mixtures, such as LiC(CF3SO2)3, LiC(C2F5SO2)3, LiAsF6, LiClO4, Li2B10Cl10, and Li2B12Cl12, are illustrated. Furthermore, as an electrolyte, inorganic solid electrolytes, such as the gel-like polymer electrolyte which sank the electrolytic solution into polymer electrolytes, such as polyethylene oxide, polyacrylonitrile, and polyvinylidene fluoride, and LiI, Li3N, are illustrated. The electrolyte of the lithium secondary battery of this invention can be used without restrictions, unless Li compound as a solvent which makes ion conductivity discover, and the solvent which dissolves and holds this decompose on the voltage at the time of charge of a battery, electric discharge, or preservation.

[0045] As the quality of cathode active material of the lithium secondary battery of this invention Lithium content transition metal oxides, such as LiCoO2, LiNiO2, LiMn2O4, LiMnO2, LiCo0.5Ni0.5O2, and LiNi0.7Co0.2Mn0.1O2, And the metal oxide which does not contain lithium, such as MnO2, are illustrated. Moreover, in addition to this, if it is the substance electrochemically inserted and desorbed from lithium, it can use without restriction.

[0046] The lithium secondary battery according to other aspects of affairs of this invention is characterized by having the plus terminal which consists of an electrode of above-mentioned this invention, ***, and nonaqueous electrolyte. As nonaqueous electrolyte, the same thing as

the above-mentioned nonaqueous electrolyte can be used.

[0047] As the lithium metal, a lithium-titanium alloy or an aluminum-lithium alloy, etc., can be used, for example.

[0048]

[Mode for carrying out the invention] It is possible to change suitably and to carry out in the range which the invention is not hereafter limited to the following work examples at all through this invention is explained still in detail based on a work example, and does not change the summary.

[0049] [Experiment 1]

[Production of ***] The thin film was formed by the RF sputtering method on the electrolysis copper foil (using electrolysis copper foil (18 micrometers, in thickness, surface roughness Ra = 0.188 micrometer) as a current collection object. As a thin film, the silicon-Cobalt-thin film, the silicon-chromium-thin film, and the silicon-thin film were formed. About the silicon-Cobalt-thin film, five kinds of thin films from which the content of Cobalt differs were formed.

[0050] The condition of sputtering were made into the conditions of sputtering gas (Ar) flux 100sccm, substrate temperature room temperature (with no heating), reaching pressure 0.6E-5Pa (5x10-7Torr), and the high frequency electric power 500W. As a target, the target (4 inches (100mm) in diameter) of single crystal silicon is used. The chip of Cobalt (Co) has been arranged about the thing which made Cobalt contain as a different-species element, and the chip of chromium (Cr) has been arranged on a silicon (Si) target about the thing which made chromium contain as a different-species element. The thin film was formed so that the thickness might be set to about 5 micrometers on electrolysis copper foil (100mm x 100mm).

[0051] About each obtained thin film, when the Raman spectral-couple analysis was conducted, about 480cm-1 the peak was detected, but about 520cm-1 the peak was not detected. This showed that the obtained thin film was a thin film which makes amorphous silicon a subject. Moreover, about the thin film which made Cobalt or chromium contain, a fixed quantity of content of each element was carried out by fluorescence X-line analysis. The arrangement state of the chip in the content of the different-species element in each thin film and the target in the case of sputtering is shown in Table 1.

[0052]

[Table 1]

[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]

[0053] If the content of Co in the thin film shown in Table 1 is converted into atom %, it will become 0.5 atom %, two atom %, five atom %, 11 atom %, and 24 atom %, respectively 1 weight %, 5 weight %, 10 weight %, 20 weight %, and 30weight %. Moreover, 5 weight % of Cr is 5 atom %.

[0054] The electrolysis copper foil in which the thin film was formed was started in size of 2.5cm x 2.5cm, and it dried under the 100-degree-C 2-hour vacuum. [Cobalt] [what is contained 1weight %] The thing of the amorphous silicon thin film which does not contain an electrode B1 and a different-species element for what contains an electrode A3 and the thing contained 2weight % for an electrode A2 and the thing contained 10weight %, and contains [an electrode A1 and the thing contained 5weight %] an electrode A5 and chromium for an electrode A4 and the thing contained 40weight % 5weight % was used as the electrode X1. These electrodes were used as *** in production of the following batteries.

[0055] [Production of a plus terminal] 85 weight % of LiCoO2 powder with an average particle diameter of 10 micrometers, 10 weight % of carbon powder as an electric conduction agent, and 5 weight % of polyvinylidene fluoride powder as a binder were mixed, N-methyl-2-pyrrolidone was added and kneaded into the obtained mixture, and slurry was produced. This slurry was applied to one side of the current collection object which consists of 20-micrometer-thick aluminum foil by the doctor blade method. After drying this under a 100-degree-C 2-hour vacuum, it started in size of 2.0cm x 2.0cm, and was considered as the plus terminal.

[0056] [Production of an electrolysis solution] To the solvent which mixed ethylene carbonate and diethyl carbonate by the volume ratio 3:7, LiPF6 1 mol/l] were dissolved and the electrolysis solution was produced.

[0057] [Production of a battery] The above-mentioned plus terminal and the above-mentioned *** were stuck through the product made from polyethylene fine porosity film all over the GURO box under argon gas atmosphere, and it inserted in the exterior object which consists of a laminate material made from aluminum. To this, 500micro of pouring of the above-mentioned electrolysis solution was done, and the lithium secondary battery was produced. The design capacity of a battery is 14mAh.

[0058] Drawing 1 is the top view showing the produced lithium secondary battery. As shown in drawing 1, through the separator 2 which consists of a product made from polyethylene fine porosity film, a plus terminal 1 and *** 3 are put together, and it is inserted into the exterior object 4. After inserting in the exterior object 4, an electrolysis solution is poured in and the lithium secondary battery is produced by closing the closure part 4a of the exterior object 4.

[0059] Drawing 2 is a sectional view to show the combination state of the battery in the inside of a battery. As shown in drawing 2, it is together put so that a plus terminal 1 and *** 3 may counter through a separator 2. On the plus terminal current collection object 1b which consists of aluminum in a plus terminal 1, the plus terminal active material layer 1a is formed, and this

plus terminal active material layer 1a is in contact with the separator 2. Moreover, in *** 3, on the *** current collection object 3b which consists of copper, are prepared by the *** active material layer 3a, n o, and the *** active material layer 3a is in contact with the separator 2.
[0060] As shown in drawing 2 , the plus terminal tab 1c which consists of aluminum for external extraction is attached to the plus terminal current collection object 1b. Moreover, the *** tab 3c which also becomes the *** current collection object 3b from nickel for external extraction is attached.
[0061] [Measurement of a charge-discharge cycle characteristic] The charge-discharge cycle characteristic was evaluated about each above-mentioned battery. Charge was performed to 4.20V by 14mA constant current, and it went the constant potential charge of Cycle 4.20V to 0.7mA. Moreover, discharge carried out in to 2.75V by 14mA constant current, and made this 1 cycle. It asked for the capacity maintenance rate after 50 cycles from the following formulas. A result is shown in Table 2. In addition, measurement was performed at 25 degrees C.
[0062] capacity maintenance rate (%) =(electric discharge capacity of electric discharge capacity / 1 cycle eye of 50 cycle eye) x100 -- the result depended on X-ray diffraction analysis (XRD; line source CuKalpha) of the thin film formed in each electrode was shown in Table 2 again.
[0063]
[Table 2]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
A1	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
A2	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
A3	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
A4	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
A5	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
B1	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
X1	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[0064] In the battery using the electrode B1 which contained the battery and chromium using the electrodes A1-A5 which contained Cobalt one to 20weight % -5weight % so that clearly from Table 2 it turns out that the capacity maintenance rate is high and the charge-discharge cycle characteristic is improving compared with the battery using the electrode X1 of the amorphous silicon thin film which does not contain the different species element.
[0065] In the electrode A5, the peak of silicon and the intermetallic compound of Cobalt is accepted with the thin film as a result of X-ray diffraction analysis. On the other hand, in electrodes A1-A4, it turns out that the peak of such an intermetallic compound is not accepted but Cobalt forms silicon and a solid solution in a thin film. In an electrode B1, it turns out similarly that chromium forms silicon and a solid solution with a thin film.
[0066] [Experiment 2] The thin film was formed by the RF sputtering method on electrolysis copper foil like the experiment 1. As a thin film, a silicon alloy thin film (a silicon iron thin film, a

silicon nickel thin film. A silicon JIRUKONIUMU thin film, a silicon silver thin film, a silicon manganese thin film, a silicon molybdenum thin film, a silicon tantalum thin film, the silicon niobium thin film, the silicon titanium thin film, the silicon tungsten thin film, and the silicon vanadium thin film were formed.

[0067] As a target, the chip of the above-mentioned different species element was arranged and used on the single crystal silicon target like the experiment 1. The size and number of sheets of each chip are shown in Table 3. It checked that it was the thin film which contains the Raman spectroscopic analysis and makes amorphous silicon a subject about each obtained thin film.

[0068] Using the electrolysis copper foil in which the thin film was formed, the lithium secondary battery was produced like the experiment 1, and the charge-discharge cycle characteristic was evaluated like the experiment 1. A result is shown in Table 3. In addition, the result of the lithium secondary battery using the comparison electrode X1 in experiment 1 is also collectively shown in Table 3.

[0069]

[Table 3]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
C	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
D	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
E	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
F	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
G	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
H	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
I	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
J	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
K	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
L	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
M	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
N	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
X1	-	-	-	[illegible]	[illegible]	[illegible]	[illegible]	

[0070] About electrode C-N shown in Table 3, the relation between weight % and atomic % is shown in Table 4.

[0071]

[Table 4]

[illegible]	[illegible]	[illegible]	
		[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]

[0072] [The battery using electrode C-N using the amorphous silicon thin film which made the different species element contain according to this invention] so that clearly from Table 3 it turns out that the capacity maintenance rate is high and the charge-discharge cycle characteristic is improving compared with the battery using the electrode X1 of the amorphous silicon thin film which does not contain the different species element. Moreover, since the peak of the intermetallic compound of silicon and a different species element is not accepted into the thin film as a result of X-ray diffraction analysis, it turns out that the different-species element forms silicon and a solid solution in a thin film.

[0073] Also in the above-mentioned different-species element, electrode C-H containing zinc, iron, nickel, JIRUKONIUMU, silver, and manganese shows the good capacity maintenance rate, and especially zinc, iron, JIRUKONIUMU, and nickel show the good capacity maintenance rate of 85% or more also in the.

[0074] (Experiment 3) The thin film was formed by the sputtering method which used DC pulse discharge on the electrolysis copper foil, using electrolysis copper foil (18 micrometers in thickness, surface roughness Ra = 0.188 micrometer) as a current collection object. As a thin film, the silicon Cobalt thin film, the silicon zinc thin film, the silicon iron thin film, and the silicon JIRUKONIUMU thin film were formed.

[0075] The conditions of sputtering were made into the conditions of the impressed electromotive force 1300W, sputtering gas (Ar) flow 85sccm, substrate temperature room temperature (with no heating), reaction pressure 0.532Pa (4x10-3Torr), DC pulse frequency 100kHz, and pulse width 1.856microsecond. The thin film was formed so that the thickness might be set to about 5 micrometers on the field of electrolysis copper foil (170mm x 470mm).

[0076] The silicon alloy target with a size of 10cm x 20cm obtained by mixing with silicon and sintering each element of Cobalt, zinc, iron, and JIRUKONIUMU as a target was used. The kind of mixed element in each target, concentration, and the concentration of the mixed

element in the obtained thin film were shown in Table 5. In addition, the element concentration in a thin film was measured by fluorescence X-ray analysis.
[0077] Moreover, about each obtained thin film, the Raman spectroscopic analysis was conducted and it checked that it was the thin film which makes amorphous silicon a subject. Using the electrolysis copper foil in which the thin film was formed, the lithium secondary battery was produced like the experiment 1 and the experiment 2, and the charge-discharge cycle characteristic was evaluated like the experiment 1 and the experiment 2. A result is shown in Table 5. In addition, the comparison electrode X2 which formed the amorphous silicon thin film as comparison using crystalline silicon as a target was produced. The result of the lithium secondary battery using the comparison electrode X2 is also collectively shown in Table 5.
[0078]
[Table 5]

[illegible]	[illegible]				[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]				
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
X2	-	-		-	[illegible]	[illegible]	[illegible]	-

[0079] The battery using electrode O-S using the amorphous silicon thin film which made the different-species element contain according to this invention, so that clearly from Table 5, it turns out that the capacity maintenance rate is high and the charge-discharge cycle characteristic is improving compared with the battery using the electrode X2 of the amorphous silicon thin film which does not contain the different-species element formed on the same conditions. Moreover, into the thin film, the peak of the intermetallic compound of silicon and a different-species element was not accepted as a result of X-ray diffraction analysis. Therefore, it turns out that the different-species element forms silicon and a solid solution in a thin film.
[0080] About Electrode O, it is at the end time of 4 cycles, it took out, and SEM observation was performed. The break which uses the trough of unevenness on the surface of a thin film as an end over the whole thin film was formed in the thickness direction, and the result checked that the thin film was separated by this break pillar shaped.
[0081] Moreover, Si weight per unit area made a fixed quantity by fluorescence X-line analysis was standardized by film thickness, and it asked for the weight density of Si per cm3 volume. In the electrode X2, in spite of having contained Co and [illegible] weight % [illegible] as compared with Electrode O

to having been 2.22g/cm3. It was 2.13g/cm3. Even if this adds Cobalt, it shows that the fall of the weight density of Si and atomic density is controlled.
[0082] Furthermore, the electric discharge capacity density per unit volume is the range from which the good cycle characteristic is acquired, and since it is more possible to consider it as the active material layer of a narrower area and thinner thickness as the value rises in size, it is an important value on the design of a battery. The electric discharge capacity density per unit volume was 6.8Ah/cm3 both the electrode X2 and the electrode O. That is, in spite of containing Cobalt 20weight % (11 atom %) in Electrode O, electric discharge capacity comparable as an electrode X2 is obtained. This shows that the degree of precision of the thin film of an active material is improving in Electrode O with the above-mentioned result.
[0083] Moreover, the electric discharge capacity density per unit volume of Electrode P is 6.3Ah/cm3, and was falling a little compared with the electrode X2. However, Electrode P is containing Cobalt 30weight % (17 atom %), and the high value is acquired if this is taken into consideration. Moreover, the capacity maintenance rate is high and the cycle characteristic is improving sharply.
[0084]
[Effect of the Invention] According to this invention, electric discharge capacity is high and it can be considered as the electrode for lithium secondary batteries excellent in the charge-discharge cycle characteristic.

[Translation done.]